regions where phosphate protonation occurs, the simultaneous repression of the free ligand levels, also through protonation, causes the concentrations of the bis species to drop to negligible levels (see the distribution curves given in Figure 2). Similarly, the mono Schiff base complexes are unstable in the pH region where the phosphate group acquires a second proton (pH $\sim$1.6), so Zn(PLP·L)H$_3^+$ is not observed.

The ionization of the pyridinium group of pyridoxal shows interesting differences between the various species.[8,10] In pyridoxal itself the p$K_a$ of this group is 8.5 but drops to 5.9 in the protonated Schiff base complex, PLGH$_2$. The value rises to 7.3 when zinc replaces the imine proton to give Zn(PL·G)H$^+$. Changes of a similar qualitative nature are expected for the pyridinium group in the PLP system. That is, the ionization of the pyridinium group of uncomplexed PLP would appear to lie at a value higher than 7.3 which is observed in the Schiff base complexes. Similar considerations can be applied to the ionization of the phosphate group. The metal ion–phosphate interactions, which appear to be present, would cause the p$K_a$ value of the phosphate group in the binary and ternary complexes to be lower than that observed for uncomplexed PLP. Thus, the phosphate group in uncomplexed PLP would appear to have a value higher than 5.5. On the basis of these assumptions, the order of ionization for uncomplexed PLP may be placed p$K_{1a}$ (H$_2$PO$_4^-$), p$K_{2a}$ (phenol), p$K_{3a}$ ($^-$HPO$_4^-$), and p$K_{4a}$ (pyridinium). This order places the ionization of the PLP phenol group (p$K_{2a}$ = 3.63) closer to the value (p$K_{1a}$ = 4.25)[8] assigned to the phenol group of PL and brings the ratio of the phosphate ionization constants more in line with the value of 10$^5$ observed for phosphoric acid. This order is similar to that proposed by Anderson and Martell[22] with the exception of the interchange of the monohydrogen phosphate and phenol groups.

The distribution curves for zinc(II) in some of the titrations obtained here are given in Figure 2. It can be seen that protonated species predominate at pH 7 with the unprotonated forms becoming increasingly important as the pH increases slightly above neutrality. These distribution curves are very similar to those found for pyridoxal.[10] The chief differences between the two systems arise from the presence of Zn(PLP)H$_i^{i-1}$ ($i$ = 0, 1, 2) species, which become less important above pH 5, and Zn(PLP·L)H$_2$, which becomes important below pH 6.5. Thus, there is not a marked increase in complexity of the systems when PLP–metal ion systems themselves are studied rather than seemingly simpler metal ion–PL systems. Considering PL hemiacetal formation, PLP may actually be preferable under many circumstances.

---

# Studies on Nitrogen-Coordinated Complexes. Preparations and Reactions of Hydrido–Phosphine Complexes of Ruthenium and Rhodium

**Takashi Ito, Shoji Kitazume, Akio Yamamoto, and Sakuji Ikeda**

*Contribution from the Research Laboratory of Resources Utilization,*
*Tokyo Institute of Technology, Meguro, Tokyo, Japan.*
*Received September 2, 1969*

**Abstract:** Tetrakis(triphenylphosphine)ruthenium dihydride, H$_2$Ru(PPh$_3$)$_4$, and tetrakis(triphenylphosphine)rhodium hydride, HRh(PPh$_3$)$_4$, were synthesized by the reaction of MCl$_3$ or M(acac)$_3$ (M = Ru and Rh), triphenylphosphine, and Et$_3$Al in THF. Both light yellow complexes were characterized by means of elemental analyses, thermal decompositions, infrared spectroscopy, and other chemical reactions. H$_2$Ru(PPh$_3$)$_4$ was found to dissociate in solution into free triphenylphosphine and H$_2$Ru(PPh$_3$)$_3$, and the reversible combination of H$_2$Ru(PPh$_3$)$_3$ with N$_2$ and H$_2$ was demonstrated. In the exchange reaction with deuterium, 24–25 hydrogens per mole of the ruthenium complex were found to participate, indicating the reversible exchange of all the *ortho* hydrogens of phenyl groups with deuterium, whereas in the rhodium complex, the number of exchangeable hydrogens was about seven to nine. The reactions of the ruthenium complex with TCNE gave (TCNE)$_3$Ru(PPh$_3$)$_2$, whereas acrylonitrile was polymerized to high polymer by the complex.

The study of the nitrogen-coordinated transition metal complexes is now becoming one of the most attractive subjects with special reference to the mechanistic investigation of ammonia producing reactions by the systems composed of transition metal compounds and reducing agents[1] or by biological systems.[2]

A variety of transition metal systems which can combine with molecular nitrogen through reactions with organic nitrogen compounds[3–8] or with atmospheric nitrogen[9–19] have been reported.

---

[1] (a) M. E. Volpin, M. A. Ilatovskaya, L. V. Kosyakova, and V. B. Shur, *Chem. Commun.*, 1074 (1968), and references therein; (b) G. Henrici-Olivé and S. Olivé, *Angew. Chem.*, **79**, 898 (1967); (c) E. E. van Tamelen, G. Boche, S. W. Ela, and R. B. Fechter, *J. Amer. Chem. Soc.*, **89**, 5707 (1967); (d) E. E. van Tamelen, G. Boche, and R. Greeley, *ibid.*, **90**, 1677 (1968); (e) H. Brintzinger, *ibid.*, **88**, 4305, 4307 (1966); (f) *Biochemistry*, **5**, 3947 (1966); (g) R. Maskill and J. M. Pratt, *Chem. Commun.*, 950 (1967).

[2] See, for example, R. W. F. Hardy and R. C. Burns, *Ann. Rev. Biochem.*, **37**, 331 (1968).

[3] (a) J. P. Collman and J. W. Kang, *J. Amer. Chem. Soc.*, **88**, 3459 (1966); (b) J. P. Collman, M. Kubota, J.-Y. Sun, and F. Vastine, *ibid.*,

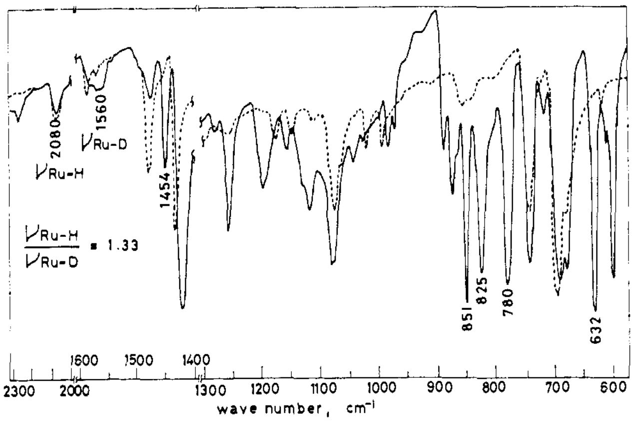


Figure 1. Infrared spectra (KBr) of $H_2Ru(PPh_3)_4$ (dotted line) and the product of the exchange reaction of $H_2Ru(PPh_3)_4$ with deuterium (solid line).

As an extension of our work on nitrogen tris(triphenylphosphine)cobalt hydride,[10] we discovered that a similar ruthenium complex, tetrakis(triphenylphosphine)ruthenium dihydride, combines with nitrogen in a benzene solution at room temperature.[15] Divalent ruthenium complexes coordinated with $N_2$ are known,[4a,b,6,8,9] but no instance of a reversible combination of $N_2$ with a ruthenium complex had been reported. The nitrogen-coordinated ruthenium complex, the presence of which we confirmed in solution, was recently isolated *via* a different route by Knoth.[16]

This report relates to the synthesis of the dihydridoruthenium complex, $H_2Ru(PPh_3)_4$, and of the hydridorhodium complex, $HRh(PPh_3)_4$, which has been briefly communicated previously[15] and to the reactions of these complexes with gaseous nitrogen, hydrogen, deuterium, and some other vinyl compounds.

## Results and Discussion

Yellow crystals of tetrakis(triphenylphosphine)ruthenium dihydride, $H_2Ru(PPh_3)_4$, and tetrakis(triphenylphosphine)rhodium hydride, $HRh(PPh_3)_4$, were prepared, by methods similar to the synthesis of nitrogen tris(triphenylphosphine)cobalt hydride,[10a] from ruthenium(III) chloride or ruthenium(III) acetylacetonate and rhodium(III) chloride or rhodium(III) acetylacetonate, respectively. The metal salts were reduced with triethylaluminum in the presence of triphenylphosphine in benzene or tetrahydrofuran in an atmosphere of nitrogen at room temperature.

$$RuX_3 + PPh_3 + AlEt_3 \longrightarrow H_2Ru(PPh_3)_4$$

$$RhX_3 + PPh_3 + AlEt_3 \longrightarrow HRh(PPh_3)_4$$

$$X = Cl^- \text{ or acetylacetonato anion}$$

The characterization of the diamagnetic complexes was accomplished by means of infrared spectroscopy, elemental analysis, and chemical reactions as described below.

**Characterization of the Ruthenium Complex. Infrared Spectrum.** The infrared spectrum of the ruthenium complex (KBr disk) showed a band at 2080 cm$^{-1}$, which was assigned to Ru-H stretching vibration, along with the characteristic bands ascribable to triphenylphosphine (Figure 1). A part of the band at 2080 cm$^{-1}$ was shifted to 1560 cm$^{-1}$ ($\nu_{Ru-D}$) by an exchange reaction of the complex with deuterium as shown in Figure 1. These spectral results indicate that the complex possesses triphenylphosphine as ligand and has a hydride structure.

**Chemical Properties.** The number of hydrogen atoms attached to the central metal atom was decided by means of chemical reactions. By thermal decomposition up to 200°, gaseous hydrogen and benzene were evolved and the amount of $H_2$ evolved was 40% of the theoretical value for $H_2Ru(PPh_3)_4$. On acidolysis, as little as 30% $H_2$ was also evolved. On reaction of the complex with an excess amount of iodine, hydrogen was released which amounted to 83% of the theoretical and a brown complex $RuI_3(PPh_3)_3$ was obtained, whereas in the reaction with iodine in a ratio of 2:1, 21% $H_2$ was evolved and purple crystals of composition $HRuI(PPh_3)_3$ were obtained. By reaction of ethyl bromide in benzene solution, ethylene and ethane (1:33) were evolved, and purple crystals which were identified as $HRuBr(PPh_3)_3$ by elemental analysis and the infrared spectrum were isolated.

The bulk of chemical evidence as a whole supports the dihydrido structure, $H_2Ru(PPh_3)_4$, which satisfies the 18-electron rule and is considered most reasonable for the diamagnetic complex. Similar dihydride phosphine complexes have been reported recently, and a detailed nuclear magnetic resonance study has been made.[20] Although the *cis*-dihydro structure was assumed to explain the infrared spectrum of the diphenylmethylphosphine complex which showed two $\nu_{Ru-H}$ bands at 1940 and 1885 cm$^{-1}$,[20] our complex showed a single Ru-H stretching band at 2080 cm$^{-1}$, suggesting

---

**89**, 169 (1967); (c) J. P. Collman, M. Kubota, F. D. Vastine, J.-Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, **90**, 5430 (1968).

(4) (a) A. D. Allen and C. V. Senoff, *Chem. Commun.*, 621 (1965); (b) F. Bottomley and S. C. Nyburg, *ibid.*, 897 (1966); (c) A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu, and C. V. Senoff, *J. Amer. Chem. Soc.*, **89**, 5595 (1967); (d) A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967).

(5) (a) L. Yu. Ukhin, Yu. A. Shvetzov, and M. L. Khidekel, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 957 (1967); (b) Yu. G. Borod'ko, V. S. Bukreev, G. I. Kozub, M. L. Khidekel, and A. E. Shilov, *Zh. Strukt. Khim.*, **8**, 542 (1967).

(6) J. Chatt and J. E. Fergusson, *Chem. Commun.*, 126 (1968).

(7) H. A. Scheideggar, J. N. Armor, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 3263 (1968).

(8) L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *ibid.*, **90**, 5295 (1968).

(9) (a) A. E. Shilov, A. K. Shilova, and Yu. G. Borod'ko, *Kinetikai Kataliz*, 7, 768 (1966); (b) Yu. G. Borod'ko, A. K. Shilova, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **176**, 1297 (1967).

(10) (a) A. Yamamoto, S. Kitazume, L. S. Pu, and S. Ikeda, *Chem. Commun.*, 79 (1967); (b) A. Yamamoto, L. S. Pu, S. Kitazume, and S. Ikeda, *J. Amer. Chem. Soc.*, **89**, 3071 (1967); (c) L. S. Pu, A. Yamamoto, and S. Ikeda, *ibid.*, **90**, 7170 (1968).

(11) (a) A. Misono, Y. Uchida, and T. Saito, *Bull. Chem. Soc. Jap.*, **40**, 700 (1967); (b) A. Misono, Y. Uchida, T. Saito, and K. M. Song, *Chem. Commun.*, 419 (1967); (c) A. Misono, Y. Uchida, M. Hidai, and T. Kuse, *ibid.*, 981 (1968); (d) A. Misono, Y. Uchida, M. Hidai, and M. Araki, *ibid.*, 1044 (1968).

(12) A. Sacco and M. Rossi, *ibid.*, 316 (1967); *Inorg. Chim. Acta*, **2**, 127 (1968).

(13) J. H. Enemark, B. R. Davis, J. A. McGinnety, and J. A. Ibers, *Chem. Commun.*, 96 (1968).

(14) (a) D. E. Harrison and H. Taube, *J. Amer. Chem. Soc.*, **89**, 5706 (1967); (b) D. E. Harrison, E. Weissberger, and H. Taube, *Science*, **159**, 320 (1968).

(15) A. Yamamoto, S. Kitazume, and S. Ikeda, *J. Amer. Chem. Soc.*, **90**, 1089 (1968).

(16) W. H. Knoth, *ibid.*, **90**, 7172 (1968).

(17) A. D. Allen and F. Bottomley, *Can. J. Chem.*, **46**, 469 (1968).

(18) (a) A. Sacco and M. Aresta, *Chem. Commun.*, 1223 (1968); (b) C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito, and M. G. Swanwick, *J. Organometal. Chem.*, **14**, 349 (1968).

(19) P. W. Jolly and K. Jonas, *Angew. Chem.*, **80**, 705 (1968).

(20) K. C. Dewhirst, W. Keim, and C. A. Reilly, *Inorg. Chem.*, **7**, 546 (1968).

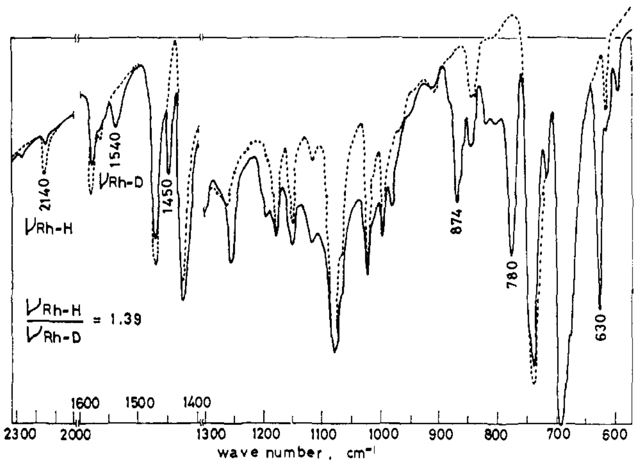


Figure 2. Infrared spectra (KBr) of $HRh(PPh_3)_4$ (dotted line) and the product of the exchange reaction of $HRh(PPh_3)_4$ with deuterium (solid line).

the *trans*-dihydro structure. We assume that the difference in the structure of these hydride complexes may, though it is yet uncertain, come from the difference in the method of preparation.

**Characterization of the Rhodium Complex. Infrared Spectra.** The solid-phase infrared spectrum (KBr disk) of the rhodium complex is very similar to that of the ruthenium complex as shown in Figure 2. A Rh-H stretching vibration appeared, in this case, at 2140 $cm^{-1}$ which shifts to 2147 $cm^{-1}$ in a Nujol mull. It can be seen in the figure that most of the band at 2140 $cm^{-1}$ was shifted to 1540 $cm^{-1}$ ($\nu_{Rh-D}$) by allowing the complex to react with deuterium.

**Chemical Properties.** The complex liberates only a trace of $H_2$ on pyrolysis up to 200°; however, 79% of the theoretical amount of $H_2$, calculated on the basis of the structure $HRh(PPh_3)_4$, was evolved on acidolysis by 50% sulfuric acid. The reaction of the complex with excess iodine afforded a trace of $H_2$ and brown crystals, which were identified as $RhI_2(PPh_3)_2$ by elemental analysis. By a substitution reaction with 1,2-bis(diphenylphosphino)ethane (DPPE), the complex was converted to $HRh(DPPE)_2$, the infrared spectrum of which shows $\nu_{Rh-H}$ at 1907 $cm^{-1}$ in a Nujol mull. This value is in fair agreement with that already reported for the same complex prepared *via* a different route.[21]

From the evidence mentioned above, the complex was identified as $HRh(PPh_3)_4$. This complex was prepared independently by Takesada, *et al.*,[22] and Keim[20,23] *via* different methods. The good agreement of the melting point (162–163°) and of the frequency value of $\nu_{Ru-H}$ with a reported value[20,22,23] indicate the identity of the compound.

**Reactions of $H_2Ru(PPh_3)_4$ with Nitrogen and Hydrogen.** When nitrogen is passed through a benzene solution of $H_2Ru(PPh_3)_4$ at room temperature, the red color of the solution turns brownish and a sharp infrared band appears at 2143 $cm^{-1}$. This band disappears on passing argon through the solution at room temperature and is accompanied by a color change of the solution from brown to red. The cycle can be repeated many times. A part of the band at 2143 $cm^{-1}$ was shifted to 2110 $cm^{-1}$ when the reaction was carried out with nitrogen containing $^{29}N_2$. From these results and from the comparison with other $N_2$ complexes, we assigned the band at 2143 $cm^{-1}$ to the N-N stretching vibration of a $N_2$ ligand coordinated to the metal.

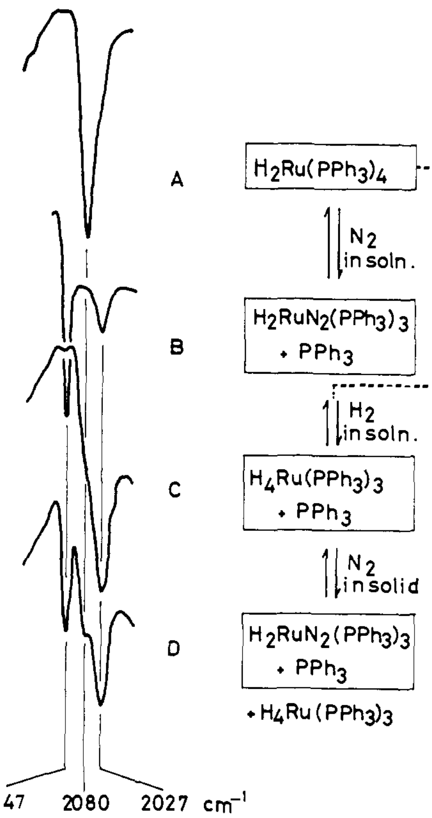


Figure 3. Infrared spectrum (KBr) in the region of 2000–2200 $cm^{-1}$ with various treatments of the ruthenium complex: (A) $H_2Ru(PPh_3)_4$; (B) freeze-dried after the introduction of $N_2$ into the benzene solution of A; (C) freeze-dried after the introduction of $H_2$ into the benzene solution of A; (D) C was contacted with $N_2$ in solid phase.

The addition of excess triphenylphosphine to the benzene solution interferes with the combination of molecular nitrogen; the more triphenylphosphine that is added to the solution, the weaker the band at 2143 $cm^{-1}$ becomes. This fact suggests the presence of the following equilibrium.

$$H_2Ru(PPh_3)_4 + N_2 \rightleftharpoons H_2RuN_2(PPh_3)_3 + PPh_3 \qquad (1)$$

$H_2Ru(PPh_3)_4$ is considered to dissociate in the solution to free triphenylphosphine and $H_2Ru(PPh_3)_3$ which is capable of combining with molecular nitrogen. The addition of excess triphenylphosphine may cause the shift of the above equilibrium to the left, thus preventing the combination of $N_2$ with the ruthenium complex.

The following results substantiate the above assumption. A brownish white powder was obtained by freeze-drying the benzene solution which was swept with $N_2$. An infrared spectrum of the powder in KBr disk indicated bands at 2147 and 2027 $cm^{-1}$ (Figure 3B). Assuming the equilibrium of eq 1, we can expect the powder to be a mixture of the nitrogen-ruthenium complex, $H_2RuN_2(PPh_3)_3$, and free triphenylphosphine. If this is the case, two bands at 2147 and 2027 $cm^{-1}$ should be ascribed to $\nu_{N-N}$ and $\nu_{Ru-H}$, respectively.

---

(21) A. Sacco and R. Ugo, *J. Chem. Soc.*, 3274 (1964).
(22) M. Takesada, H. Yamazaki, and N. Hagihara, *Bull. Chem. Soc. Jap.*, 41, 270 (1968).
(23) W. Keim, *J. Organometal. Chem.*, 8, 25 (1967).

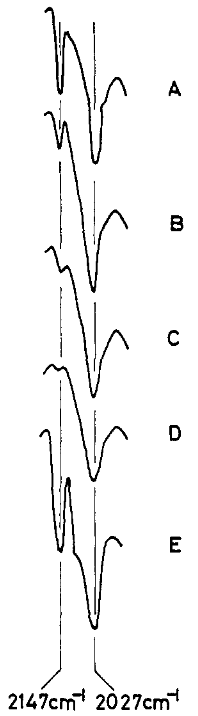


Figure 4. Changes in the intensity of $\nu_{N-N}$ with the time of evacuation: (A) just after the freeze-drying was finished; (B) after evacuation for 10 hr; (C) 15 hr; (D) 20 hr; (E) $N_2$ was contacted with D.

These assignments were confirmed by the fact that when hydrogen, instead of nitrogen, was introduced to the solution, the infrared spectrum of the freeze-dried powder showed a large band at 2027 $cm^{-1}$ and no indication of the other band (Figure 3C). In this case the following equilibrium should be anticipated as an analogy of the reaction with nitrogen.

$$H_2Ru(PPh_3)_4 + H_2 \rightleftharpoons H_4Ru(PPh_3)_3 + PPh_3 \qquad (2$$

That the $N_2$ ligand is very loosely bound to the complex makes the isolation of $H_2RuN_2(PPh_3)_3$ very difficult. The $N_2$ ligand on the ruthenium complex can be removed by prolonged evacuation at room temperature as shown in Figure 4 by the decrease of the band at 2147 $cm^{-1}$ with time, while the band at 2027 $cm^{-1}$, due to $\nu_{Ru-H}$, remains unchanged. At this point, the initial $H_2RuN_2(PPh_3)_3$ is considered to be converted to $H_2Ru(PPh_3)_3$ which has the $\nu_{Ru-H}$ band at the same frequency with $H_2RuN_2(PPh_3)_3$. This concept was substantiated by the reappearance of the band at 2147 $cm^{-1}$ by contacting the last complex in a solid phase with gaseous $N_2$ for about 2 weeks (Figure 4E).

The solid-phase reaction of the complex with $N_2$ was also observed in the tetrahydrido complex. $H_4Ru(PPh_3)_3$, which exists in the system, partly changes to $H_2RuN_2(PPh_3)_3$ in the solid phase by replacing two hydridic hydrogens with atmospheric nitrogen (Figure 3C,D).

Although the isolation of the nitrogen-coordinated ruthenium complex from the solid mixture of freeze-dried powder was unsuccessful because of the highly labile character of the $N_2$–Ru bond as mentioned above, the relative intensity of the band at 2147 $cm^{-1}$ could be increased by washing the mixture with *n*-hexane at −40° (Figure 5). When the mixture was washed at room temperature, the resulted complex was again $H_2Ru(PPh_3)_4$. A slight dissolution of the $N_2$-coordinated complex in solution may cause the recombination of free triphenylphosphine with the ruthenium complex by reaction 1, thus producing $H_2Ru(PPh_3)_4$.

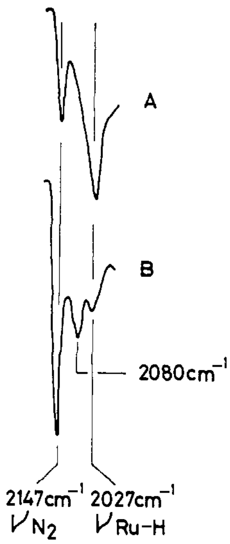


Figure 5. $\nu_{N-N}$ and $\nu_{Ru-H}$ of the freeze-dried mixture before (A) and after (B) washing with *n*-hexane at 40°. The band at 2080 $cm^{-1}$ was ascribed to $\nu_{Ru-H}$ of $H_2Ru(PPh_3)_4$ to which the $N_2$ complex was partially converted by washing.

Following our previous short communication,[15] Knoth isolated the $N_2$-coordinated complex, $H_2RuN_2(PPh_3)_3$, *via* a different route, from the reaction of $HRuCl(PPh_3)_3$ with triethylaluminum and nitrogen.[16] The infrared spectral observation that the $\nu_{N-N}$ appears at 2147 $cm^{-1}$ (in a Nujol mull) agrees well with our result. However, the presence of two $\nu_{Ru-H}$ bands at 1947 and 1917 $cm^{-1}$ differs from our result. We assume that this disagreement may come from the difference in the configurations which may depend upon the route of preparation.

The infrared spectrum of $H_4Ru(PPh_3)_3$ in solution showed a $\nu_{Ru-H}$ band at 1910 $cm^{-1}$ as described in the preceding paper.[15] Considerable shift of the band to 2027 $cm^{-1}$ was observed when the spectrum was taken in solid state.

Attempts to prepare similar nitrogen-coordinated complexes of rhodium have been unsuccessful.

**Reactions of $H_2Ru(PPh_3)_4$ and $HRh(PPh_3)_4$ with Deuterium.** In the course of our study on the reaction of the $N_2$-coordinated cobalt complex, we obtained an unpublished result that not only the hydrogen atom of Co–H but also hydrogens of phenyl groups in triphenylphosphine can participate in the exchange reaction between the complex and deuterium. The same result was independently reported by Parshall.[24] By an equilibrium experiment, he found that 19 hydrogens per mole of cobalt complex took part in the exchange reaction with deuterium in benzene solution at 25°. From the infrared and nuclear magnetic resonance spectral evidence, the elucidation was made that a rapid equilibrium occurs in which the *ortho* C–H bonds add to the cobalt complex and then 18 *ortho*-hydrogen atoms of the phenyl rings can, along with a hydridic hydrogen, have a chance of exchanging with $D_2$.[24]

---

(24) G. W. Parshall, *J. Amer. Chem. Soc.*, **90**, 1669 (1968).

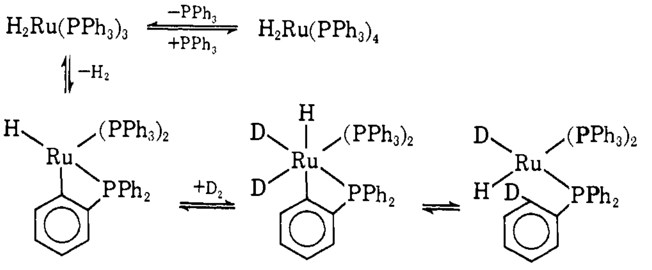
When the ruthenium complex, $H_2Ru(PPh_3)_4$, in benzene solution was allowed to equilibrate with a large excess of deuterium at 25°, at a pressure of 252 mm, it was found that the extent of the exchange corresponded to about 24–25 hydrogens per mole of the complex (Table I). The number of the exchanged H atoms was calculated from the fraction of H atoms in the gas phase of the system. An infrared spectrum of the resulting complex (Figure 1) shows that $\nu_{Ru-H}$ at 2080 $cm^{-1}$ is partly shifted to 1560 $cm^{-1}$ which was assigned to $\nu_{Ru-D}$ ($\nu_{Ru-H}/\nu_{Ru-D} = 1.33$) and that several new strong bands appeared in the region 780–900 $cm^{-1}$ which are ascribable to out-of-plane deformation vibrations of di- and/or trisubstituted benzene. Furthermore, the nuclear magnetic resonance spectrum in $C_6D_6$ solution of triphenylphosphine oxide which was recovered by decomposing the resulted complex with 30% $H_2O_2$ indicates a characteristic *ortho*-dideuterated phenyl structure (Figure 6).[24] Thus, we assume, in analogy with the cobalt nitrogen complex, that a rapid equilibrium involving insertion of the Ru complex into *ortho* C–H bonds may be taking place (Scheme I).

**Table I.** Exchange Reactions of $H_2Ru(PPh_3)_4$ and $HRh(PPh_3)_4$ with $D_2$[a]

| Complex, mmol | $D_2$, mmol | Gas composition, %[b] $D_2$ | HD | $H_2$ | No. of exchanged H atoms[c] |
|---|---|---|---|---|---|
| $H_2Ru(PPh_3)_4$, 0.0417 | 4.01 | 77.8 | 19.2 | 3.0 | 24–25 |
| $HRh(PPh_3)_4$, 0.0766 | 5.23 | 89.2 | 9.1 | 1.7 | 7–9 |

[a] Reactions were carried out in sealed systems in benzene solution at room temperature for 10 days. [b] Final gas composition calculated from mass spectral data. [c] Number of exchanged H atoms per mole of complex.

Scheme I



By the similar reaction of the rhodium complex $HRh(PPh_3)_4$ with deuterium, the number of hydrogen atoms in the complex exchanged with deuterium was found to be only about 7–9 in contrast with the case of the ruthenium and cobalt complex (Table I). The infrared spectrum of the resulting complex shows a $\nu_{Rh-D}$ band at 1540 $cm^{-1}$ ($\nu_{Rh-H}/\nu_{Rh-D} = 1.39$) and two new bands at 780 and 874 $cm^{-1}$ (Figure 2). These results suggest that the *ortho* protons can take part in the exchange reaction with deuterium to some extent, but a certain effect (presumably, steric effect) may hinder the participation of all of the *ortho* protons.

**Reactions of $H_2Ru(PPh_3)_4$ with Tetracyanoethylene and Acrylonitrile.** A certain hydrido-transition metal complex is known to act as a starting material or as a reactive intermediate in the hydrogenation reaction of olefins. In the course of our preliminary study on the attempted isolation of substituted or unsubstituted olefins with the ruthenium complex, we found the following two extreme cases: the reaction with tetracyanoethylene (TCNE) afforded a stable, substituted complex, whereas rapid polymerization occurred by the reaction with acrylonitrile.

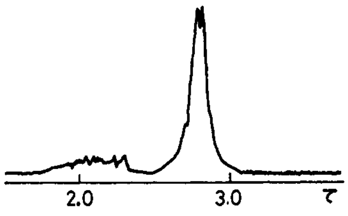


Figure 6. Nmr spectrum of deuterated triphenylphosphine oxide at 60 Mc in a $C_6D_6$ solution with tetramethylsilane as internal standard.

By the reaction of $H_2Ru(PPh_3)_4$ with an excess of tetracyanoethylene in benzene solution at room temperature, a blue-black complex immediately precipitated. This complex, which was recrystallized from a mixture of N,N-dimethylformamide and diethyl ether, showed very strong bands at 2212 and 1648 $cm^{-1}$ ascribed to $\nu_{C\equiv N}$ and $\nu_{C=C}$, respectively, along with the phenyl bands in the infrared spectrum (KBr disk). Considering the result of elemental analysis, the blue-black complex, which has high thermal stability (no change was observed up to 300°), was assigned to $(TCNE)_3Ru(PPh_3)_2$.

Acrylonitrile polymerizes rapidly affording polyacrylonitrile by the complex even at −20°. The viscosity-average molecular weight of the polymer obtained at 20° was about 81,000. This is, to our knowledge, the first example of a polymerization reaction initiated by a hydrido–transition metal complex.

## Experimental Section

**Reagents.** Ruthenium trichloride was prepared from $RuCl_3 \cdot 3H_2O$ by dehydration with $SOCl_2$.[25] Rhodium trichloride was of commercial origin. Ruthenium(III)[26] and rhodium(III)[27] acetylacetonates were prepared according to the literature. Triethylaluminum was used after distillation under reduced pressure. Triphenylphosphine was used as purchased, mp 80.0–81.5°. Commercially available deuterium and tetracyanoethylene (guaranteed purity) were used without further purifications. Acrylonitrile was purified and dried by the usual manner. Solvents were dried and distilled under nitrogen.

**Preparation of the Complexes.** Every operation was carried out in an atmosphere of nitrogen purified by an activated copper column, or under argon, or under vacuum.

**Tetrakis(triphenylphosphine)ruthenium Dihydride.** As a typical example, 5 g of ruthenium trichloride and 25 g of triphenylphosphine were suspended in 100 ml of tetrahydrofuran, and 13.3 ml of triethylaluminum was added to this mixture at −20°. The mixture was stirred at room temperature for a long period (about 1 week, at least) until light yellow crystals separated out completely. Ethane with a small amount of ethylene and a trace of $C_4$ hydrocarbon were evolved. The crystals were filtered and washed repeatedly with diethyl ether and *n*-hexane. The yield of the crystals was about 24% based on the ruthenium trichloride. The complex is slightly soluble in such organic solvents as benzene, toluene, tetrahydrofuran, and acetone, and can be recrystallized from these solvents at low temperature. The complex is moderately sensitive to oxygen in solid phase, but in solution it is very easily decomposed by air, mp 180° dec. *Anal.* Calcd for $C_{72}H_{62}P_4Ru$: C, 75.05; H, 5.42. Found: C, 74.91; H, 5.44.

---

(25) A. R. Pray, *Inorg. Syn.*, **5**, 153 (1957).

(26) G. A. Barbieri in "Gmelins Handbuch der Anorganischen Chemie," Vol. 63, Verlag Chemie, Berlin, 1938, p 85.

(27) R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, **84**, 2303 (1962).

**Tetrakis(triphenylphosphine)rhodium Hydride.** All the procedures employed were essentially the same as those for the preparation of the ruthenium complex. *Anal.* Calcd for $C_{72}H_{61}P_4Rh$: C, 75.0; H, 5.33. Found: C, 75.7; H, 5.54; mp 162–163°. Other properties of the complex are the same as for the ruthenium complex.

**Chemical Reactions.** All the reactions were carried out under vacuum in a Schlenk-type flask. Estimation of the amount of $H_2$ gas evolved by each reaction was performed by the use of a Toepler pump, by which the total amount of the noncondensable gas at −196° was measured; the composition of the gas was determined by mass spectroscopy.

**Reaction of $H_2Ru(PPh_3)_4$ with Iodine.** A solution of 0.40 mmol of iodine in benzene was added at room temperature to a stirred solution of 0.256 g (0.222 mmol) of $H_2Ru(PPh_3)_4$ in 30 ml of benzene in a sealed system. Additional stirring was continued for 1 hr at ambient temperature. The $H_2$ gas evolved during the reaction amounted to 0.197 mmol. The brown precipitate was separated by filtration, washed with diethyl ether, and identified as $RuI_3(PPh_3)_2$ on the basis of elemental analysis. *Anal.* Calcd for $C_{54}H_{45}I_3P_3Ru$: C, 51.1; H, 3.6; I, 30.0. Found: C, 50.2; H, 3.8; I, 31.0.

When 0.282 g (0.245 mmol) of $H_2Ru(PPh_3)_4$ was allowed to react with 0.123 mmol of iodine in the same manner as described above, the $H_2$ gas evolved during the reaction for 15 hr amounted to 0.0513 mmol and the purple crystals which were identified as $HRuI(PPh_3)_3$ on the basis of elemental analysis and infrared spectrum were isolated, $\nu_{Ru-H}$ 2020 cm$^{-1}$ (Nujol mull). *Anal.* Calcd for $C_{54}H_{46}IP_3Ru$: C, 63.8; H, 4.56; I, 12.5. Found: C, 61.9; H, 4.97; I, 12.9.

**Reaction of $H_2Ru(PPh_3)_4$ with Ethyl Bromide.** Into the benzene solution (30 ml) of $H_2Ru(PPh_3)_4$ (0.239 g, 0.208 mmol), 5 ml of $C_2H_5Br$ was added by trap-to-trap method. The evolved gas (0.019 mmol) was analyzed by gas chromatography and identified as a mixture of ethylene and ethane (molar ratio, 1:33). The purple crystals were isolated after reaction for 50 hr at room temperature and were identified as $HRuBr(PPh_3)_3$ from elemental analysis and infrared spectrum. *Anal.* Calcd for $C_{54}H_{46}BrP_3Ru$: C, 66.9; H, 4.79; Br, 8.25. Found: C, 68.6; H, 4.42; Br, 9.78.

**Reaction of $HRh(PPh_3)_4$ with Iodine.** The same method as was used for the reaction of the ruthenium complex with iodine was employed for the reaction of $HRh(PPh_3)_4$ (0.584 g, 0.506 mmol) with 0.658 mmol of iodine. $H_2$ gas (0.004 mmol) was evolved during the reaction, and a brown complex which was identified as $RhI_2(PPh_3)_2$ was isolated. *Anal.* Calcd for $C_{36}H_{30}I_2P_2Rh$: C, 49.0; H, 3.43; I, 28.8. Found: C, 48.2; H, 3.99; I, 26.9.

**Reaction of $HRh(PPh_3)_4$ with 1,2-Bis(diphenylphosphino)ethane.** Into the benzene solution (30 ml) of $HRh(PPh_3)_4$ (0.4 g, 0.347 mmol), 0.31 g (0.779 mmol) of 1,2-bis(diphenylphosphino)ethane (DPPE) was added. After stirring for 5 hr, orange-colored crystals were separated by concentrating the solution to 10 ml. The crystals were collected by filtration and washed repeatedly with diethyl ether. The yield of the crystals was practically quantitative. The structure of the crystals was assigned to $HRh(DPPE)_2$ on the basis of elemental analysis and infrared spectrum, $\nu_{Rh-H}$ 1907 cm$^{-1}$ (Nujol mull).

$$HRh(PPh_3)_4 + 2DPPE \longrightarrow HRh(DPPE)_2 + 4PPh_3$$

*Anal.* Calcd for $C_{52}H_{49}P_4Rh$: C, 70.1; H, 5.34. Found: C, 70.9; H, 5.66.

**Reaction of $H_2Ru(PPh_3)_4$ with Nitrogen.** On passing purified nitrogen through a red solution of $H_2Ru(PPh_3)_4$ in benzene at room temperature, a color change of the solution to brown was observed in a few minutes. The brownish color reverts to red by bubbling argon through the solution. Attempts to isolate the nitrogen-coordinated ruthenium complex were made by freeze-drying the benzene solution containing the complex and free triphenylphosphine. Though the $\nu_{N-N}$ band appeared in the infrared spectrum of the powder thus obtained, and the intensity increased by washing the powder with *n*-hexane at −40°, complete purification of the complex (free from the mixed triphenylphosphine) was unsuccessful as judged from elemental analysis of nitrogen.

**Reactions of $H_2Ru(PPh_3)_4$ and $HRh(PPh_3)_4$ with Deuterium.** A flask containing a benzene solution of the weighed sample of the ruthenium complex (0.0417 mmol) was connected to a vacuum line which was connected to a mercury manometer. After degassing the solution completely by the freeze–thaw method, deuterium (4.01 mmol) was introduced into the system and the amount of $D_2$ gas was determined by means of the manometer. The reaction was continued for 10 days at room temperature with vigorous stirring; the contents of the flask was frozen by liquid nitrogen. A noncondensable gas at −196° in the system was submitted to mass spectral analysis (Table I). The resulting complex was isolated by freeze-drying from the solution and the infrared spectrum was observed.

**Reactions of $H_2Ru(PPh_3)_4$ with Olefinic Compounds. 1. Tetracyanoethylene.** A solution of $H_2Ru(PPh_3)_4$ (0.277 mmol) in 20 ml of benzene was degassed and combined with tetracyanoethylene (1.39 mmol) at room temperature *in vacuo.* The red color of the solution rapidly changed to deep blue-black and a precipitate with the same color separated out. The evolution of $H_2$ (0.0243 mmol) by the reaction was confirmed by mass spectroscopy. The solution was allowed to stand at room temperature overnight, and the resulting blue-black solid was collected by filtration under nitrogen. The solid was washed repeatedly with diethyl ether and *n*-hexane and purified by recrystallization from a DMF–ether mixture; 0.1581 g of the purified compound was obtained (about 57% yield as $(TCNE)_3Ru(PPh_3)_2$). The infrared spectrum (KBr) of the compound showed strong bands at 2212 and 1648 cm$^{-1}$, together with the characteristic bands of triphenylphosphine. The compound is rather stable in air and did not melt up to 300°. *Anal.* Calcd for $C_{54}H_{30}N_{12}P_2Ru$: C, 64.22; H, 2.99; N, 16.65. Found: C, 64.23; H, 3.69; N, 16.02.

**2. Acrylonitrile.** To the weighed sample of $H_2Ru(PPh_3)_4$, degassed acrylonitrile was charged by the trap-to-trap method. Abrupt polymerization reaction took place immediately after the temperature of the mixture was raised up to room temperature. When the mixture was allowed to stand at −20°, the polymerization was completed in 1 day. The resulting polymer was dissolved in DMF and purified by repeated reprecipitation from a DMF–methanol system. The infrared spectra (KBr) of the polymers were essentially identical with that obtained by radical polymerization of acrylonitrile. The intrinsic viscosity $[\eta]$ of the polymer obtained at room temperature was 1.58 (at 25°, in DMF solution) which corresponds to a molecular weight of 81,000.[28]

**Analyses.** a. Infrared spectra were measured by Shimadzu IR-27 C, Hitachi EPI-G3, and Perkin-Elmer 125 spectrometers. Every preparation of the sample was performed under $N_2$.

b. The mass spectral analysis was performed with a Hitachi RMU-5B spectrometer by Mr. H. Sakurai of Tokyo Institute of Technology, to whom the authors are very grateful.

c. Nmr spectra were measured by a JEOL C-60 spectrometer with tetramethylsilane as the internal standard.

d. The microanalysis was performed by Mr. T. Saito of Tokyo Institute of Technology, to whom the authors are very grateful.

**Acknowledgment.** The authors are indebted to Mr. Akira Aoki for experimental assistance.

---

(28) J. Bisschops, *J. Polymer Sci.*, 17, 81 (1955).